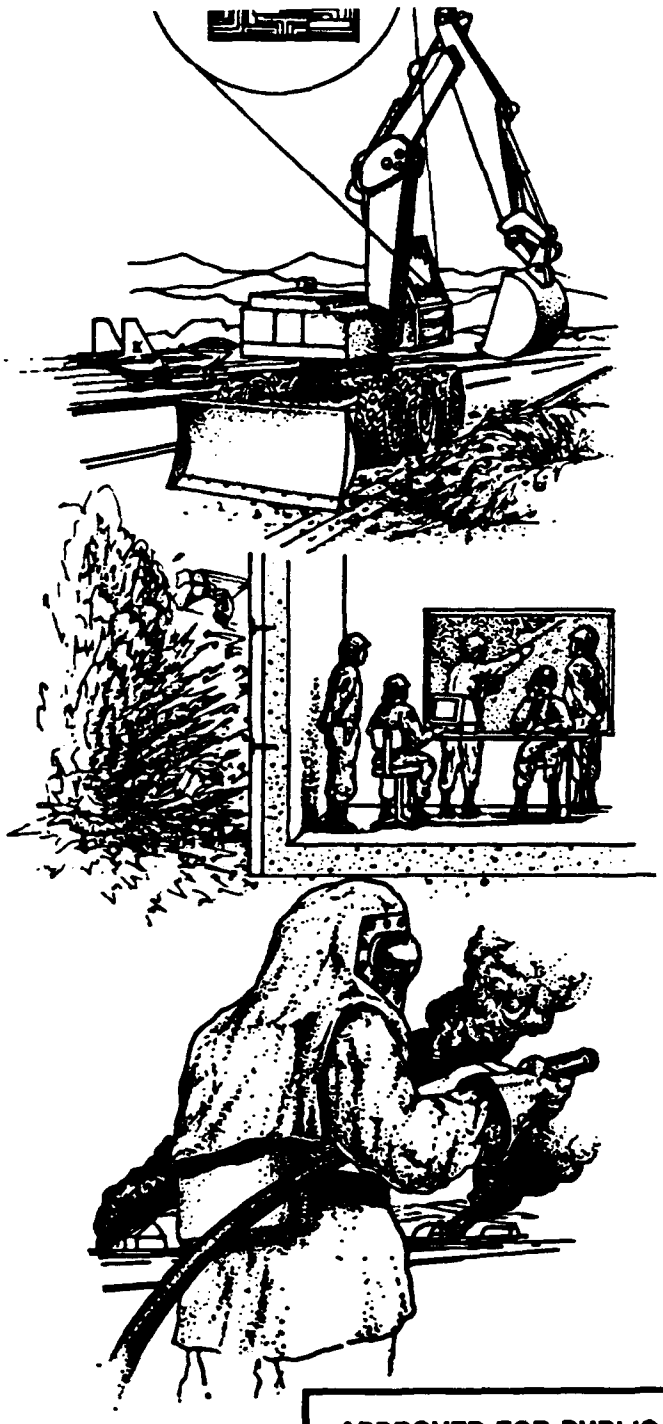
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ESL-TR-87-03



NEXT-GENERATION FIRE EXTINGUISHING AGENTS PHASE IV — FOUNDATION FOR NEW TRAINING AGENT DEVELOPMENT

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DECEMBER 1989

INTERIM REPORT

JULY 1988 — DECEMBER 1989

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91-16562

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 1989	Interim Report July 1988-December 1989

4. TITLE AND SUBTITLE
NEXT-GENERATION FIRE EXTINGUISHING AGENTS PHASE IV -- FOUNDATION FOR NEW TRAINING AGENT DEVELOPMENT

5. FUNDING NUMBERS
F29601-C-87-0001

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
SS 2.06(1)

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Engineering and Services Laboratory
Air Force Engineering and Services Center
Tyndall Air Force Base, Florida 32403

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ESL-TR-87-03

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The objective of the overall effort is to originate concepts for a next-generation suppressant for multidimensional fires. The objective of the Phase IV effort was to provide a foundation for the development of an agent to substitute for Halon 1211 in Air Force firefighter training. Toxicity and environmental data on selected candidate training agents were surveyed and compiled. Hydrochlorofluorocarbons (HCFCs), chlorofluorocarbons (CFCs), and blends of these materials were tested on small-scale through medium-scale outdoor fires of JP-4. The results of this phase indicate that a blend of CFCs or HCFCs could provide a replacement for Halon 1211 in firefighter training.

14. SUBJECT TERMS
Halon, CFC, Chlorofluorocarbon, HCFC, Hydrochlorofluorocarbon, Ozone, Fire extinguishment

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	Unclassified	Unclassified	Unclassified

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort is to originate concepts for a next-generation suppressant for multidimensional fires. The objective of the Phase IV effort was to provide a foundation for the development of an agent to substitute for Halon 1211 in Air Force firefighter training.

B. BACKGROUND

Halon fire extinguishing agents have excellent dimensionality and they are clean; however, they give poor security and have poor deliverability, particularly outdoors with adverse winds. Moreover, halons have unacceptable environmental impacts. A particularly serious environmental problem is the suspected impact of common halon agents (Halons 1211 and 1301) on stratospheric ozone.

In Phase I, a study of flame suppression and fire extinguishment concepts was performed. A recommendation was made in the Phase I report that research efforts emphasize halons and halon-like materials. In Phase II, development of a program to find chemical alternatives for halons was initiated. The Phase II effort included both basic and applied laboratory studies of suppression mechanisms and extinguishment with an emphasis on Halon 1211 alternatives. In Phase III, an effort to develop a new firefighter training agent having a reduced ozone impact was initiated.

C. SCOPE

The scope of the overall project is to originate concepts for new fire extinguishing agents. In Phase IV, toxicity and environmental data on recommended training agents were surveyed and compiled. The review considered Ozone Depletion Potentials (ODPs), boiling point, and toxicity. In addition, general information on ODP, terrestrial environmental

characteristics, and toxicity of halocarbons was reviewed. HCFC-22, HCFC-123, and blends of the two were tested on small-scale outdoor fires of JP-4 fuel. Pure CFC-114 and a commercially available blend of CFC-11, CFC-12, CFC-113, and CFC-114 were tested on medium- and large-scale outdoor fires.

D. METHODOLOGY

Saturated halocarbons with significant toxicity data available were reviewed. These agents have the best chance of being introduced in the near future. The fire extinguishment testing used extinguishers of the type that are used for Halon 1211 alternatives. The testing was performed using JP-4 fuel in outdoor pits. Such tests are standard for comparison of halon-like agents.

E. TEST DESCRIPTION

Outdoor fire extinguishment testing used JP-4 fuel floating on water. The surface areas were 1, 4, 28, and 150 ft^2. Standard portable extinguishers were manually operated to discharge test materials onto burning fuel. In some cases, special nozzles were designed and used.

F. RESULTS

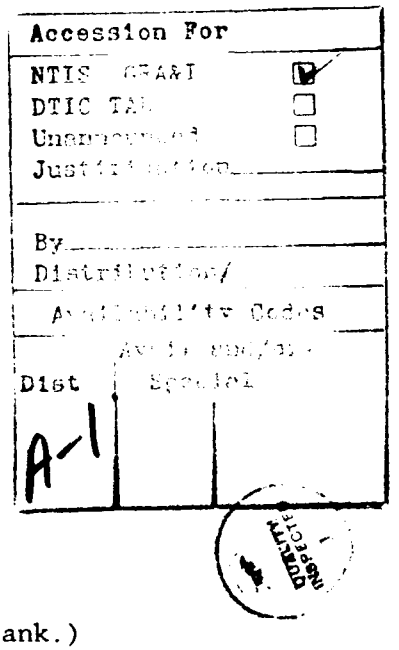
The review of selected commercially available materials revealed a number of halocarbons that have ODPs lower than those of the halons and that could be considered as firefighter training agents. Many of these have relatively low toxicities. The fire extinguishment testing showed that HCFC-123 can extinguish fires; the addition of HCFC-22 decreases the fire extinguishment capability. All of the CFCs (chlorofluorocarbons) exhibited significant fire suppression capabilities; however, these materials have significant ODPs.

G. CONCLUSIONS

This experimental work indicates that a decreased vapor pressure significantly improves agent performance. Evidence of this improved performance is seen in the better extinguishment by HCFC-123 alone than in a blend with HCFC-22. Similarly, the fire suppression ability of a CFC blend having a relatively low vapor pressure is good to very good in field tests. The extinguishing ability of the blend improves as the fire size increases, as a consequence of the fuel inerting, discharge, and flame penetrating properties of this agent. On the other hand, the blend lacks rapid fire knockdown capability. Since halocarbons will generally have low ODPs if their molecules contain one or more hydrogen atoms bonded to carbon, HCFCs are good prospects for alternative agents.

H. RECOMMENDATIONS

A computerized database of halocarbons should be prepared to aid in screening, prioritizing, and selecting candidate chemicals. Work should be continued on prediction of fire extinguishment and ODP from molecular structure. Additional work on predicting and categorizing toxicities of candidate agents is needed. Work on alternative training agents should be broken out as a separate program.



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PREFACE

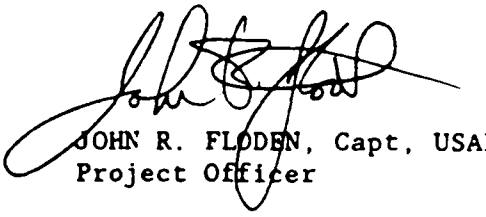
This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico, Albuquerque, New Mexico 87131, under contract F29601-87-C-0001, for the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403.

This report summarizes work done between July 1988 and December 1988. The HQ AFESC/RDCF Project Officers were Major E. Thomas Morehouse and Capt. John R. Floden.

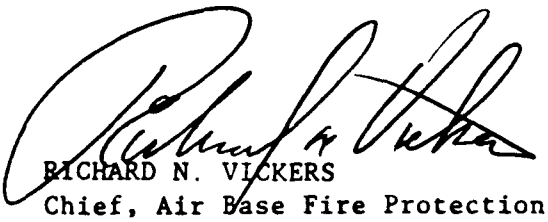
Dr. Mary Ann Smith of the College of Pharmacy, University of New Mexico, served as the toxicology consultant on this project.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

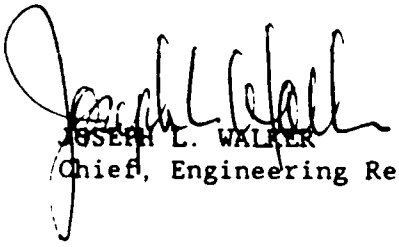
This technical report has been reviewed and is approved for publication.



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LIST OF ABBREVIATIONS

AFB	Air Force Base
ALC	Approximate Lethal Concentration
BCFC	bromochlorofluorocarbon
BFC	bromofluorocarbon
CAH	Composite Advanced Halon
CERF	Civil Engineering Research Facility
CFC	chlorofluorocarbon
CNS	Central Nervous System
EPA	Environmental Protection Agency
FC	fluorocarbon
HAS	Hardened Aircraft Shelter
HBFC	hydrobromofluorocarbon
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HMIS	Hazardous Materials Identification System
LLNL	Lawrence Livermore National Laboratory
NAPL	nonaqueous phase liquid
NASA	National Aeronautics and Space Administration
NMERI	New Mexico Engineering Research Institute
ODP	Ozone Depletion Potential
OSHA	Occupational Safety and Health Administration
PCE	perchloroethylene
PEL	Permissible Exposure Limit
QSAR	Quantitative Structure Activity Relationship
SBUV	Solar Backscatter Ultraviolet

LIST OF ABBREVIATIONS
(CONCLUDED)

STEL	Short Term Exposure Limit
TCA	trichloroethane
TCE	trichloroethylene
TLV	Threshold Limit Value
TWA	Time-Weighted Average
U. L.	Underwriter's Laboratory
UNEP	United Nations Environmental Program

SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of the total effort is to originate concepts for a next-generation suppressant for multidimensional fires and to analyze both the molecular basis for the agent action and the quantitative burning inhibition obtained. The objective of the Phase IV effort is to provide a foundation for the development of an agent to substitute for Halon 1211 in Air Force firefighter training.

B. BACKGROUND

Although many new types of fire suppressants have been originated, improved agents are still needed. Recently a major problem has arisen with one of the most important classes of firefighting agents, the halons. Halons 1301 and 1211, the most widely used halon extinguishants, are believed to deplete stratospheric ozone.

In Phase I, a study of flame suppression and fire extinguishment concepts was performed (Reference 1). A recommendation was made in the interim report that research efforts emphasize halons and halon-like materials (i.e., halocarbons). Toward the end of the Phase I study, it became increasingly apparent that halon firefighting agents, like chlorofluorocarbons (CFCs), were depleting stratospheric ozone. Accordingly, a high priority was given to the development of clean fire extinguishants to replace halons.

In Phase II, development of a program to find chemical alternatives for Halons 1211 and 1301 was initiated (Reference 2). Since the greatest need within the Air Force is a replacement for Halon 1211, the clean agent used for aircraft fires and the fire protection system planned for the Hardened Aircraft Shelter (HAS), emphasis was placed on Halon 1211 alternatives.

Halon 1301 replacements were not, however, totally ignored. The Phase II effort consisted primarily of laboratory studies. During this effort it became increasingly apparent that halons might be banned entirely owing to their impact on stratospheric ozone.

In Phase III, an effort to develop a new firefighter training agent, one with a reduced ozone impact, to replace Halon 1211 was initiated (Reference 3). This phase emphasized small-scale testing and primarily encompassed known materials with significant toxicity and environmental impact data available.

Both laboratory- and small-scale discharge extinguishment test apparatuses and procedures were developed during Phase III. These tests will be optimized in future work on halon replacements.

The Phase III work showed that concentrations required for extinguishment by halocarbons containing only chlorine and fluorine as the halogen substituents were higher than those of the halons (which contain bromine). The work also indicated that this higher extinguishment concentration could be offset by improved streaming performance by the agent. Halocarbons with good streaming properties are promising candidates for fire suppressants. Accordingly, chlorofluorocarbons or their blends can be considered for testing as alternative training agents. Note, however, that any materials containing compounds regulated under the Montreal Protocol are probably acceptable only as temporary alternative agents.

C. SCOPE

The scope of the overall project includes the origination of concepts for new fire extinguishing agents. The concepts may involve any combination of inhibitors that act by chemical and/or physical mechanisms or by new modes of utilization. Hypotheses are tested using laboratory-scale experiments. Fire parameters are monitored throughout the testing to provide information concerning mechanisms of action and to permit feedback

for refinement of original concepts and origination of new concepts. Sufficient research to determine the molecular mechanisms of extinguishment of selected agents is also performed. The next-generation agent(s) should be able to suppress one-, two-, or three-dimensional fires with minimal application under a range of ambient conditions. The final product of this project is a technical report detailing all work accomplished, with conclusions and recommendations.

D. TECHNICAL APPROACH

The following tasks are required for Phase IV of this project:

Medium- and large-scale pool fire tests shall be performed on promising candidate agents. Toxicity and environmental data on recommended training agents will be surveyed and compiled.

The contractor shall provide a task/milestone report at the completion of Phase IV to include the test results, conclusions, and recommendations concerning the performance of the agent. The report shall also include future development work required or advisable to produce an acceptable agent.

SECTION II
TRAINING AGENT CANDIDATES

A. HALOCARBON NOMENCLATURE

Firefighting agents can suppress fires by physical and/or chemical mechanisms. The primary chemical mechanism is the elimination of high-energy species (primarily atomic hydrogen, atomic oxygen, and hydroxyl free radicals) that sustain combustion. Halogenated hydrocarbons are the only clean fire extinguishing chemicals that derive a significant portion of their fire suppression capability from a chemical mechanism.

Halocarbons are compounds containing carbon atoms bonded to one or more atoms of fluorine, chlorine, bromine, and/or iodine (halogen atoms). Admittedly, some doubt exists about the relative importance of chemical and physical extinguishment mechanisms for these compounds, in particular for compounds containing only fluorine as the halogen substituent (fluorocarbons); however, it is generally accepted that the elimination of free radicals during combustion provides a major pathway for extinguishment for most halocarbons.

Compounds containing other elements in addition to carbon, hydrogen, and halogens can exhibit fire extiguishment capabilities; however, for the present, such compounds will not be considered. Thus, such compounds as haloethers and halocarboxylic acids are not discussed here. Even with this limitation, halocarbons include several types of compounds that differ according to the structure of the carbon backbone. The most important division is between compounds containing carbon-carbon multiple bonds (aromatics, alkenes, and alkynes) and those containing only single carbon-carbon bonds (alkanes). The former compounds are said to be "unsaturated"; the latter are "saturated." Since many unsaturated halocarbons have known or suspected toxicity problems, only saturated halocarbons are considered in the present phase of the Next-Generation Fire Extinguishing Agent project.

In Phases II and III of this project (References 2 and 3), some halocarbons containing no bromine were found to provide sufficient fire extinguishment capabilities that they could be considered as candidate halon replacements. Many of these chlorine- and fluorine-containing halocarbons have complex chemical names. A simple nomenclature system, the Freon designations, has been developed by workers at du Pont. In this system, the first number of the designation gives the number of carbon atoms minus 1, the second number, the number of hydrogen atoms plus 1, and the third number, the number of fluorine atoms. Leading or trailing zeros are dropped. Thus, for example, Freon-11 refers to trichlorofluoromethane, CCl_3F. A lower case letter may be added as a suffix when several isomers are possible. A suffix containing an upper case "B" denotes bromine substituents.

Since "Freon" is a commercial trademark, it is now accepted practice to use other prefixes. Unfortunately, this causes complications. The prefix "CFC" is very often used. For example, Freon-11 is now more commonly called CFC-11. However, since "CFC" denotes "chlorofluorocarbon," many feel that it should not be used for compounds containing hydrogen in addition to chlorine and fluorine. Such compounds are often referred to as "HCFCs" (hydrochlorofluorocarbons). Similarly, compounds containing only fluorine as the halogen substituent are called "FCs" (fluorocarbons), and those containing hydrogen and fluorine, "HFCs" (hydrofluorocarbons). No universally accepted practice exists, however.

Workers in the refrigeration industry have avoided the problem by using the generic prefix "R." For example, the compound R-11 is the same as CFC-11. The prefix "R," however, denotes "refrigerant," and many of the compounds of interest have never been considered as refrigerants. Moreover, several halocarbon refrigerant mixtures have been given R-prefixed numbers that have no direct relationship to the chemical composition.

Despite the complexity of the system, designations using prefixes "CFC," "HCFC," etc. will be used in this and future reports.

Compounds containing bromine atoms will usually be given halon designations, a nomenclature system described in the report for Phase II of this project (Reference 2). Though the halon names are much easier to use, they are ambiguous and fail to distinguish between isomers. The commercially available halons are often given CFC names by the chemical industry: Halon 1301 is CFC-132B1, Halon 1211 is CFC-12B1, Halon 2402 is CFC-114B2, and Halon 1202 is CFC-12B2. However, this practice is avoided in reports originating from this project. Normally, no hyphen is used in the halon names. The word "halon" is capitalized only when it is used with a number in designating a specific compound.

Note that bromine containing fluorocarbons compounds may be referred to as "BFCs" (bromofluorocarbons, e.g., Halons 1301 and 2402), "BCFCs" (bromochlorofluorocarbons, e.g., Halon 1211), "HBFCs" (hydrobromofluoro-carbons), etc.

B. COMMERCIALLY AVAILABLE MATERIALS

The availability of commercial chemicals as replacements for Halon 1211 in firefighter training would accelerate work to obtain an alternative training agent. Table 1 contains a list of CFCs and related materials which are or have been made in commercial quantities. For comparison, this table also contains information on halon fire extinguishing agents. The ODP (Ozone Depletion Potential) is discussed further along in this section.

Compounds outside of those listed in Table 1 are also being considered as candidate alternative training agents; however, available materials, particularly those produced in large volume, warrant special attention. Note, however, that Table 1 is not limited to large-volume substances.

TABLE 1. HALOGENATED HYDROCARBONS.

Common name	Formula	Boiling point, °C	ODP[a]	Formula weight
CFC-11	CCl_3F	23.8	1.00	137.37
CFC-12	CCl_2F_2	-29.8	0.90	120.91
CFC-13	$CClF_3$	-81.4	0.34	104.46
FC-14	CF_4	-128.0	0	88.00
HCFC-21	$CHCl_2F$	8.9	0.01	102.92
HCFC-22	$CHClF_2$	-40.8	0.04	86.47
HF-23	CHF_3	-82.0	0	70.01
CFC-112	$C_2Cl_4F_2$	92.8	1.42	203.83
CFC-113	$C_2Cl_3F_3$	47.6	1.09	187.38
CFC-114	$C_2Cl_2F_4$	3.8	0.93	170.92
CFC-115	C_2ClF_5	-39.1	0.47	154.47
FC-116	C_2F_6	-78.2	0	138.01
Halon 1301	$CBrF_3$	-57.7	14.28	148.91
Halon 1211	$CBrClF_2$	-3.3	2.64	165.36
Halon 2402	$C_2Br_2F_4$	47.3	11.7	259.82

[a]Per-molecule Ozone Depletion Potential as calculated by Lawrence Livermore National Laboratory.

C. TOXICITY

1. Health Effects

Two types of acute health effects are known for halogenated hydrocarbons (Reference 4). First, they can cause Central Nervous System (CNS) responses such as dizziness, impaired coordination, and anesthesia. Second, inhalation of halogenated hydrocarbons can cause cardiac arrythmia and cardiac sensitization to adrenalin. Cardiac arrhythmias and CNS effects are often readily reversible upon termination of exposure; however, both can lead to death with excessive exposure.

In addition, two types of long-term or chronic health effects are important for halocarbons. First, halocarbons commonly exhibit hepatotoxicity; they can cause liver damage, particularly with long-term exposure. Second, like many other chemicals, some halocarbons are carcinogenic (cancer-causing).

2. Toxicity Rating Systems

A toxicity rating system and an efficient approach to toxicity information research are essential to halon replacement work. Among the sources of toxicity information are government reports, private industry reports, journal publications, and texts. On-line computer searches permit rapid retrieval of data from these sources. The on-line Chemical Abstracts (CA) data base, maintained by the American Chemical Society, is being used in the present halon replacement work to access much of the toxicity information. Using the on-line CA file and matching up chemical compounds with topics (e.g., "chlorodifluoromethane" and "toxicity"), one can find articles from 1970 to the present containing the required information. The on-line CAOLD file gives information about articles written between 1962 and 1966. The on-line CA registry file gives registry numbers for specific compound names and structures for more exact searching.

An accurate, consistent toxicity rating system must be created from the compiled toxicity information. Existing toxicity rating systems provide a good starting point.

Underwriter's Laboratories' toxicity rating system, created in 1967, is based on tolerable substance concentration levels on a scale of 1 to 6, with 6 denoting the lowest toxicity (Table 2). This classification system is primarily descriptive of acute toxicities. The U. L. classifications of the materials listed in Table 1 are given in Table 3.

TABLE 2. ABSTRACTED U. L. CLASSIFICATIONS OF COMPARATIVE LIFE HAZARDS.[a]

Group	Gas or vapor concentration, %	Exposure duration	Effect	Example
1	0.5 - 1	5 min	death; serious injury	SO_2
2	0.5 - 1	30 min	death; serious injury	CH_3Br
3	2 - 2.5	1 hr	death; serious injury	CH_2BrCl
4	2 - 2.5	2 hr	death; serious injury	CH_3Cl
[c]5a	--	--	--	CFC-11
[c]5b	--	--	--	C_2H_6
6	20	2 hr	no injury	CFC-12

[a]Taken from Reference 5.

[b]Group 5a is comprised of gases or vapors much less toxic than Group 4 but somewhat more toxic than Group 6.

[c]Group 5b is comprised of gases or vapors for which available data would allow classification as either 5a or 6.

TABLE 3. U. L. TOXICITY CLASSIFICATIONS OF SELECTED FLUOROCARBONS.[a]

Fluorocarbon	Formula	U. L. Group
CFC-11	CCl_3F	5a
CFC-12	CCl_2F_2	6
CFC-13	$CClF_3$	[b] 6
FC-14	CF_4	[b] 6
HCFC-21	$CHCl_2F$	[c] 4 - 5
HCFC-22	$CHClF_2$	5a
HFC-23	CHF_3	[b] 6
CFC-112	$C_2Cl_4F_2$	[b,d] 4 - 5
CFC-113	$C_2Cl_3F_3$	[c] 4 - 5
CFC-114	$C_2Cl_2F_4$	6
CFC-115	C_2ClF_5	6
FC-116	C_2F_6	[b] 6
Halon 1301	$CBrF_3$	6
Halon 1211	$CBrClF_2$	5a
Halon 2402	$C_2Br_2F_4$	5a

[a]Taken from Reference 5.

[b]Not tested by U.L; however, estimated to be in the U. L. Group noted.

[c]Much less toxic than Group 4 but somewhat more toxic than Group 5.

[d]CFC-112 appears to classify as somewhat less toxic than U. L. Group 4.

The Hazardous Materials Identification System (HMIS) is another toxicity classification system. This system classifies substance toxicity on a scale of 1 to 4, where "4" denotes the highest toxicity. The HMIS is too imprecise for useful toxicity description for the present work.

Of particular interest are the toxicity indexes for inhalation, the primary mode for exposure by compounds having high vapor pressures, a characteristic of most halocarbons. Several indexes have been established to characterize the toxicity of a gaseous material (Reference 6).

a. The LC_N is the Lethal Concentration, N percent kill, the concentration of gaseous materials that is lethal to N percent of species in a group. Normally N is 50. The units of an LC_N value are usually percent or ppm by volume. Lethal concentration refers to inhaled quantity, whereas lethal dose (LD_N) refers to quantity administered by any mode other than inhalation.

b. The ALC is the Approximate Lethal Concentration, the approximate concentration of material that would prove lethal for a given inhalation time. The ALC values may or may not give a percent kill.

c. The OSHA PEL value is the Permissible Exposure Limit as defined by the U. S. Occupational Safety and Health Administration (Reference 7). This is an 8-hour time-weighted average unless otherwise stated.

d. The TLV is the Threshold Limit Value and gives the upper allowable concentration limit of a toxic material. These values are established by the American Conference of Governmental Industrial Hygienists (Reference 8) and are based on the best available information from industrial experience, experimental animal studies, and human studies.

Three types of TLVs are used:

(1) The TLV-TWA is the Threshold Limit Value - Time Weighted Average, the highest permissible average concentration for a normal 8-hour workday and 40-hour workweek. At this concentration and under these conditions, no adverse effects are expected. A TLV-TWA is quite similar to a PEL, although the two are defined by different organizations.

(2) The TLV-STEL is the Threshold Limit Value - Short Term Exposure Limit, the concentration to which exposure for a short period of time is possible without serious effects (irritation, tissue damage, or significant narcosis). The TLV-STEL is for a 15-minute exposure, which should neither be repeated more than four times per day nor occur at time intervals shorter than 60 minutes. Often, TLV-STEL values are unknown; however, they can be predicted from the following excursion limit recommendation (Reference 8). "Short-term exposures should exceed three times the TLV-TWA for no more than a total of 30 minutes during a work day and under no circumstances should they exceed five times the TLV-TWA, provided that the TLV-C is not exceeded" (Reference 8, p. 5).

(3) The TLV-C value is the Threshold Limit Value - Ceiling, a concentration that should not be exceeded.

e. The term "ED_N" refers to the effective dose affecting N percent of a population for a given response.

Unfortunately, no general rating system is available using one or a few indexes to describe relative toxicities. Often, the ratings are for different modes of administration, different species, and different physiological effects. Initial screening and testing prioritization of candidate materials would be greatly accelerated if a few simple indexes allowing direct and rapid comparisons of halocarbon toxicities were available.

D. ENVIRONMENTAL ANALYSIS

1. Ozone Depletion

The following discussion is based on information collected toward the beginning of Phase IV of this project. Although this information is correct in generalities, details may have changed. The Phase V report will update the ozone depletion problem.

CFCs and halons are implicated in both global warming (the greenhouse effect) and depletion of stratospheric ozone. The ozone problem appears to be more tractable and amenable to resolution than the greenhouse problem since manufacture and distribution of CFCs and halons are controlled by a single industry. The international community, under the auspices of the United Nations Environmental Program (UNEP), has developed an international agreement (the Montreal Protocol) to restrict production of ozone-depleting materials. An excellent, but early, overview of both global warming and stratospheric ozone depletion is contained in Reference 9. The following discussion concerns only the ozone depletion problem; global warming will be discussed in future reports.

Because halons and fully halogenated halocarbons are extremely stable, a percentage of these molecules can pass through the troposphere without destruction to enter the stratosphere. In the stratosphere, they photolyze in the intense solar radiation to release halogen atoms. Atomic chlorine and bromine catalyze the decomposition of triatomic ozone into diatomic oxygen. The catalytic cycle is shown in Reactions [1] and [2] (Reference 10).* In these equations, X = Cl, Br, NO, and OH; however, only the cases where X = Cl or Br are of interest here.

*For the convenience of the reader, reaction numbers are placed in brackets and equation numbers are placed in parentheses throughout this report.

$$X + O_3 \rightarrow XO + O_2 \quad [1]$$

$$XO + O \rightarrow X + O_2 \quad [2]$$

The result of Reactions [1] and [2] is the formation of diatomic oxygen from monoatomic oxygen and ozone:

$$O + O_3 \rightarrow 2\ O_2 \quad [3]$$

Since an oxygen atom, a precursor for ozone, is removed with each ozone molecule, the net effect is removal of two ozone molecules in each cycle.

This process is catalytic since Br or Cl used in Reaction [1] is reformed in Reaction [2]. A single molecule of chlorine is estimated to destroy approximately 100,000 molecules of ozone before it is lost. Chlorine is eventually lost by migration of HCl molecules, which are formed by the reaction of chlorine with such species as methane, into the troposphere. In the troposphere, HCl is washed out by precipitation. Most HCl molecules, however, dissociate to reinitiate the catalytic cycle before they can drift into the troposphere.

Bromine atoms are recycled even more times than chlorine atoms because HBr molecules are less stable and dissociate more easily than do HCl molecules. Thus, halons, which usually contain bromine, are more destructive to stratospheric ozone than are CFCs containing only chlorine and fluorine substituents.

Fluorine is not considered to be significantly damaging to ozone because of the high stability of HF.

Bromine and chlorine may also have a mutually synergistic effect. This is shown in Reactions [4] through [6].

$$Cl + O_3 \rightarrow ClO + O_2 \quad [4]$$

$$Br + O_3 \rightarrow BrO + O_2 \quad [5]$$

$$BrO + ClO \rightarrow Br + Cl + O_2 \quad [6]$$

The net reaction is

$$2O_3 \rightarrow 3O_2 \quad [7]$$

If this synergism actually occurs, halons may be much more destructive than has been thought.

Owing to production and emission levels, CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) remain of greatest concern for ozone impact; however, CFC-113 ($CFCl_2CF_2Cl$), CFC-114 ($CClF_2CClF_2$), CFC-115 ($CClF_2CF_3$), methyl chloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4) also contribute significantly to predicted changes in total ozone based on their emission rates. Despite many changes in rate constants and modeling methods, the essence of the theory proposed by Molina and Rowland in 1974 (Reference 11), showing that chlorine from CFCs may significantly reduce stratospheric ozone concentrations, remains unchanged.

Two criteria determine ozone impact by a CFC or a halon: (1) relative ozone destruction efficiency and (2) emission level. Lawrence Livermore National Laboratory (LLNL) uses an atmospheric model to determine the relative impact on the ozone of a given amount of material upon release to the troposphere. This Ozone Depletion Potential, or ODP, can be calculated on either a per-molecule or per-mass basis. CFC-11 has been assigned an ODP of 1 for the purpose of comparison. The LLNL model divides the atmosphere into 44 layers from the ground to 54.25 kilometers and considers 35 species in addition to the CFCs (Reference 12). The results of early calculations using this model are shown in Table 4. Data for these types of calculations are found in References 13 and 14.

TABLE 4. STEADY-STATE MODEL WITH EMISSIONS CONSTANT AT JANUARY 1980 LEVEL.[a]

Compound	ODP[a]	Atmospheric lifetime, years	Release rate, 1000 metric tons per year	Ozone depletion, percent	Relative contribution, percent
CFC-11	1.00	63.8	272	-1.95	33.4
CFC-12	0.86	107.8	338	-2.08	35.7
CCl_4	1.11	57.0	82	-0.65	11.1
CFC-113	0.80	88.3	91	-0.52	8.9
CH_3CCl_3	0.15	9.7	476	-0.51	8.7
CFC-114	0.60	181.1	18	-0.08	1.4
HCFC-22	0.05	27.7	72	-0.03	0.5
CFC-115	0.32	385.3	4.5	-0.01	0.2

[a]Ozone Depletion Potential on a per-weight basis (Reference 12).

The depletion of stratospheric ozone is expected to cause an increase in the amount of high-energy ultraviolet radiation, UV-B, striking the earth. Preliminary data from a Solar Backscatter Ultraviolet (SBUV) instrument aboard NASA's Nimbus 7 satellite show a total global ozone decline of approximately 3 percent between 1978 (satellite launch) and 1985. At heights of 40 kilometers, where chlorine is believed to exert the greatest impact, the ozone loss seems particularly large: 12 percent by SBUV and 3 percent by ground-based Umkehr measurements.

Particularly serious is the damage to stratospheric ozone over the Antarctic. Each year since the late 1970s, at the start of the Astral spring, the ozone layer over Antartica shrinks. In October 1986, the decrease was 50 percent!

An increase in UV-B can cause damaging effects to human health, aquatic life, plants, and manmade materials. The United States Environmental Protection Agency (EPA) estimates excess cancer cases of 40 million and excess cancer deaths of 800,000 through the year 2075 due to ozone depletion.

The atmospheric concentrations of CFC-11 and CFC-12 are about 230 and 400 ppt (parts per trillion) by volume, respectively, and are increasing by 5 percent per year. An examination of current and future global production levels of the seven most important potential ozone depleters (CFC-11, CFC-12, CFC-113, carbon tetrachloride, methyl chloroform, Halon 1211, and Halon 1301) shows that the demand for these materials is likely to grow at a modest rate over the next 15 years (Reference 15).

The threat due to Halon 1211 and 1301 will increase owing to their greater ODP. Most of the Halon 1211 and Halon 1301 produced in a year is banked in the total flooding systems or other fire extinguishers. Emissions occur when the systems are activated during a fire and from system testing, filling, servicing, and leakage. Training activities are an important source of Halon 1211 emissions. The losses through accidental discharge are likely to be more significant for handheld extinguishers than for the total flooding systems. Since the halons are so expensive the amounts stored in total flooding systems are usually recovered and reused. Growth in new systems employing halons has remained high in the U.S. In 1986, it was projected that rapid growth would continue at rates averaging 15 percent through 1988. It was also projected that growth would then decline to an average of 7 percent annually until the year 2000, when the total amount of Halon 1211 and 1301 produced will be 40,800 metric tons (Reference 15). Concern for the environment has held back halon growth from these projections, and the Montreal Protocol restrictions will cause a further decrease.

An analysis of the supply, investment, and regulatory constraints that might affect CFC production until the year 2000 indicates that the demand for CFC-11 and CFC-12 is unlikely to be significantly affected in increases in raw material prices, or by threats of regulations in cases where no substitutes are readily available (Reference 16).

A number of halogenated hydrocarbons, particularly CH_3CCl_3 (HCFC-140) and CHF_2Cl (HCFC-22), react rapidly with OH radicals. This phenomenon is seen in the relatively short lifetime of 6.5 years for methylchloroform, CH_3CCl_3. For such compounds, the percentage of the molecules released at the surface that actually reach the stratosphere is strongly affected by the tropospheric OH concentration. Only molecules reaching the stratosphere can have a significant ozone impact. Unfortunately, OH concentrations in the troposphere are not well known.

Halocarbons will generally have low ODPs only if they contain some hydrogen atoms bonded to carbon atoms. This is seen in Table 1, where the ODPs for HCFC-21 and HCFC-22, whose molecules contain a single atom of hydrogen, are relatively low. Like other halocarbons containing only fluorine, CFC-14 has an ODP of zero.

2. Other Environmental Concerns

While the largest and most noticeable environmental impacts of CFCs and halons are the depletion of stratospheric ozone and global warming, they have other effects on the environment. Halocarbons often find their way into ground water and natural bodies of water through spills and by atmospheric washout due to rainfall.

The most common CFCs (CFC-11, CFC-12, CFC-113) and halons are relatively nontoxic compounds. Although in high doses these compounds have been shown to cause bronchoconstriction and heart sensitivity, no permanent damage is caused by exposure to even relatively high concentrations. CFCs and halons are generally orally nontoxic, nonmutagenic, and nonirritating to

skin and eyes of mammals (mice, rats, and rabbits). In fact, because of their high oxygen-dissolving abilities and low toxicities, perfluorocarbons are being studied as possible components of artificial blood. Little is known about the effects of CFCs and halons on fish, birds, and other wildlife.

In the environment, halogenated hydrocarbons degrade more quickly as they become more diluted and dispersed. A pool of an organic liquid (a nonaqueous phase liquid or NAPL) is relatively inert to degradation because of its low surface area and lack of exposure to oxidants and microorganisms. Once dissolved in water, a contaminant is exposed to a much wider range of degradative mechanisms. These mechanisms include hydrolysis, oxidation, dehydrohalogenation, reduction, and photodissociation. Environmental half-lives of halocarbons vary widely, from 0.01 to 1000 years, and increase as the number of halogen atoms per carbon atom increases (Reference 17).

In surface water, volatilization is considered the most significant fate of such volatile halogenated hydrocarbons as 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and perchloroethylene (PCE). The expectation of rapid evaporation of volatile compounds is supported by the fact that TCA is reported to have an evaporative half-life of 17 minutes, TCE, a half-life of 19 minutes, and PCE, a half-life of 24 minutes in slowly-stirred water starting with an initial concentration of 1 ppm (Reference 18). No great changes in evaporative half-lives are observed with the addition of small amounts of sodium chloride, dry granular bentonite clay, dry powdered dolomitic limestone, peat moss, or Ottawa silica sand.

When a chemical is introduced into the soil environment, the four processes that affect how that chemical is transported through the soil are volatilization, dispersion, adsorption, and degradation. As discussed below, volatilization, dispersion, and adsorption are the major operative mechanisms; degradation is relatively slow.

In general, CFCs and halons are highly volatile (with low boiling points and large Henry's law constants). Therefore, volatilization is the major mechanism operating for these compounds. Little information is available on the volatilization rates of organic compounds from soil. One study (Reference 19), however, shows greater than 99 percent volatilization losses for several volatile halogenated hydrocarbons. Thus, volatilization must be considered a major transport mechanism for these compounds.

A chemical in solution flowing through soil disperses due to the varying permeability of the medium, fluid mixing through pores, molecular diffusion, sorption/desorption, and reactions with soil materials. The pore structures of soil allow varying path lengths for fluid movement and mixing (hydrodynamic dispersion). If a chemical diffuses into immobile areas or closed pores, it will remain there and will be released only slowly after the concentration front has passed.

Dispersion is included in the following transport equation, which describes one-dimensional flow in a saturated, unconsolidated, homogeneous medium (References 20 through 23):

$$dc/dt = -u(dc/dx) + D(d^2c/dx^2) - (P/e)(ds/dt) + (dc/dt)_{rn} \qquad (1)$$

where c = solute concentration in aqueous phase, t = time, u = average fluid velocity, x = distance in direction of flow, D = dispersion coefficient, P = soil bulk density, e = soil porosity, S = mass of solute adsorbed per unit dry mass of soil, and rn = reaction (degradation) term.

If the above parameters are measured experimentally for actual site conditions, an estimate can be made of the rate of decrease of concentration for each compound due to dispersion. It has been found that theoretical or laboratory determinations of the value of D are not accurate for natural aquifers due to wide spatial variations in the permeability of such aquifers (Reference 21). Tracer studies must be conducted at the site to get accurate values for D.

The two main driving forces for adsorption are the hydrophobic nature of the solute and the degree of affinity of the solute for the solid surface (References 20, 24, and 25). Three types of adsorption exist: exchange, chemical, and physical. Exchange adsorption involves the attraction of opposite electrical charges, and chemical adsorption involves the formation of covalent chemical bonds to the surface. Neither of these processes occurs to any significant degree with CFCs and halons. Physical adsorption is generally weak (2 to 10 kcal/mole) and is due to van der Waals forces. Since no charges or covalent bonding is involved in adsorption of CFCs and halons, physical adsorption is the major adsorption mechanism for these compounds.

Adsorption is expressed by isotherms, the relationship of adsorbed amount Q (measured in $\mu g/g$) to concentration C_L (in $\mu g/L$). These quantities are linearly related by Henry's equation, where k is Henry's constant:

$$Q = k\ C_L \qquad (2)$$

Adsorption of organic compounds on soils correlates strongly with the soil carbon content (Reference 26). Adsorption generally increases linearly with the percentage of carbon present. Compounds with lower solubilities are usually adsorbed more strongly than those with greater solubilities.

Those compounds adsorbed most strongly will be the most persistent and spread the slowest; those adsorbed less strongly will spread faster and be dispersed more quickly. For example, CFC-11 (solubility 1100 ppm) and HCFC-21 (solubility 9500 ppm) should not be adsorbed strongly and should move relatively quickly through the soil. Because of its low solubility (170 ppm), CFC-113 should undergo significant adsorption.

In summary, because of the low toxicities and high volatilities of CFCs and halons, the environmental impacts of these materials, other than stratospheric ozone depletion and global warming, are relatively minor. Nevertheless, environmentalists are concerned about CFCs in ground water.

SECTION III
SMALL-SCALE OUTDOOR TESTS

A. OBJECTIVE

This testing, performed to determine fire extiguishment capabilities of two hydrogen-containing hydrocarbons having a low ODP, used a small-scale, 1-ft^2 fire test in an outdoor environment. The tests differed from the Phase III small-scale fire tests, which were run in an enclosure (Reference 3). The two agents tested were HCFC-22 (chlorodifluoromethane) and HCFC-123 (2,2-dichloro-1,1,1-trifluoroethane). HCFC-22 has been examined in laboratory-scale discharge extinguishment testing, where it gave fair results, and in small-scale indoor discharge extinguishment testing, where the performance was very poor (Reference 3). Very large concentrations are required for extinguishment by HCFC-22 in cup burner tests (Reference 2). HCFC-123 has not been previously tested in this project.

This study was also undertaken to determine the fire extinguishment characteristics of a mixture of HCFC-123 and HCFC-22, which had been combined to duplicate the vapor pressure of Halon 1211, thereby mimicking Halon 1211 discharge characteristics.

B. EQUIPMENT AND MATERIALS

HCFC-123 was purchased in small gas cylinders containing approximately 1 kilogram of material. HCFC-22 was transferred from a large 30-pound gas cylinder to small cylinders containing 250 to 300 grams of agent. A combination of HCFC-123 and HCFC-22 was prepared to approximate the boiling point of Halon 1211 (-3.3 ^{o}C). The composition required to produce a mixture with a boiling point near that of Halon 1211 was determined to be 0.58 mole fraction (71 percent by weight) HCFC-123 (boiling point, 28.7 ^{o}C) and 0.42 mole fraction (29 percent by weight) HCFC-22 (boiling point, -40.8 ^{o}C) to give a mixture having an approximate boiling point of -0.5 ^{o}C. Note that the boiling point of the mixture was calculated assuming ideal

behavior. Moreover, the boiling point is not constant (unless the mixture is a azeotrope) and changes as material evaporates during boiling. No azeotrope has been reported for HCFC-22 with HCFC-123; however, HCFC-22 does form an azeotrope with the similar compound 1,2-dichloro-1,2-difluoroethane (HCFC-132), which has a boiling point of 29.8 ^{o}C (Reference 27). The azeotrope contains 87.6 percent by weight HCFC-22 and has a boiling point of -41.4 ^{o}C.

Three test cylinders were evacuated and weighed, HCFC-123 was passed into each cylinder, and the cylinders were reweighed to determine the amount obtained. The amounts of HCFC-22 needed to complete each mixture were calculated and placed in the cylinders.

The fire testing was performed at the CERF/NMERI fire pad at Kirtland AFB. A square metal fire pan having an area of 1 ft^2 was filled with water, and JP-4 was floated on top. The fire was ignited with a torch and was allowed to burn for 30 seconds. Each agent was applied directly from the cylinder in a stream directed at the base of the fire. If extinguishment was not achieved, the fire was smothered and reignited before the next test. All results are given in Table 5.

In Test 5, spraying the fuel with HCFC-123 prior to ignition made initial ignition difficult. Test 6 was run with a 30-pound cylinder to make certain that the poor performance of HCFC-22 in earlier tests was not due to a drop in delivery pressure during discharge from the small cylinders used in Tests 1 and 2; however, HCFC-22 still failed to achieve extinguishment.

The performances of both pure HCFC-22 and the mixed agent were poor. Neither of these materials extinguished the fire in any test. Pure HCFC-123, on the other hand, gave a reasonable extinguishment.

TABLE 5. SMALL-SCALE OUTDOOR TESTS.

Test no.	Agent	Cylinder	Amount used, lbs	Discharge time, sec	Results
1	HCFC-22	small			No extinguishment
2	HCFC-22	small			No extinguishment
3	HCFC-123	small			Fire extinguished
4	HCFC-123	small			Fire extinguished
[a]5	HCFC-123	small			Ignition hindered
6	HCFC-22	30-lb			No extinguishment
7	HCFC-22/123	small	1.5	22	No extinguishment
8	HCFC-22/123	small	2.7	16	No extinguishment
9	HCFC-22/123	small	2.0	30	No extinguishment

[a]JP-4 surface was sprayed with HCFC-123 before ignition to determine whether any fuel inertion could be achieved.

SECTION IV
FIELD TESTS OF CFC-114

A. INTRODUCTION

These tests were run to determine the extinguishment ability of CFC-114 with medium-scale and large-scale outdoor fires. Cup burner testing showed an extinguishment concentration of 6.1 $\pm$ 0.2 percent for CFC-114, compared with 3.0 $\pm$ 0.4 percent for Halon 1211 (Reference 2). Small-scale indoor discharge tests also indicated that CFC-114 was a reasonable fire suppressant (Reference 3).

B. PROCEDURE

Three test conditions were used. For the 4-ft^2 area fires, a 2-foot square metal pan and an Amerex 9-pound extinguisher were used. For the 28-ft^2 fires, a 6-foot diameter round metal fire pan and an Amerex Model 372 20-pound (2.5-gallon) extinguisher were used. The 150-ft^2 fires were run in a 14-foot diameter round concrete fire pit. A 150-pound (10-gallon) wheeled unit was used for these large fire tests. All fires consisted of JP-4 fuel floated on water. Halon 1211 was used as a control.

C. RESULTS

The test results are shown in Table 6. In general, these results show CFC-114 to be a much poorer extinguishant than Halon 1211 under the conditions used for these tests. Note that relatively good extinguishment was obtained with CFC-114 for the large 150-ft^2 fire, where the high heat flux may have helped vaporization of this agent.

TABLE 6. FIELD-TEST RESULTS FOR CFC-114.

Test no.	Agent	Fire size, ft^2	Fuel, gal	Agent, lbs	Discharge time, sec	Extinguished	Footnote
1	CFC-114	4	1	6	14	yes	a
2	CFC-114	28	5	[c]--	30	no	b
3	Halon 1211	28	5	21.5	38	yes	d
4	Halon 1211	28	[f]--	22.5	19	yes	e
5	CFC-114	150	15	45	10	yes	g
6	Halon 1211	150	15	63	12	yes	h
7	CFC-114	28	3	20.4	--	no	i
8	Halon 1211	28	3	8.6	13	yes	i
9	CFC-114	28	3	16.3	--	no	i

[a]Wind exceeded 5 mph.

[b]Flame was off fuel, but burned back around pan lip.

[c]Not measured.

[d]Valve functioned incorrectly. Agent flow was inhibited.

[e]Wind exceeded 5 mph, laying fire over. Wind was at back of firefighter. Most fuel was burned off during test. Inertion by Halon 1211 from the previous test and lack of fuel contributed to extinguishments.

[f]No new fuel added.

[g]Fire was attacked with wind at back. Wind was approximately 5 mph.

[h]Fire was attacked at a cross wind of less than 5 mph. Fire was more vertical than in previous test.

[i]Windy. 30-second preburn.

SECTION V
FIELD TESTS OF A CFC BLEND

A. INTRODUCTION

In Phase III, laboratory tests were conducted on CAH, a commercially available blend of CFC-11, CFC-12, CFC-113, and CFC-114. This testing indicated that, in comparison with Halon 1211, CAH had poor inherent flame suppression capability as measured by extinguishment concentration but good delivery and fuel inerting characteristics. Since delivery and flame penetration properties may be as important as extinguishment concentration in determining the performance of a streaming agent, field testing was recommended. The results of this field testing are presented here.

B. PROCEDURE

Field tests were conducted at the University of New Mexico McCormick Ranch site. All tests were carried out with off-specification JP-4 fuel floated on water. A 10-second preburn was used. For the series A tests, the zero time was taken as the time of ignition. For the two other series, zero time was taken as the point at which the entire surface of the pool was covered with flame. Halon 1211 was used as a control.

A 6-foot diameter, 28.3-ft^2 area round metal pan was used in Test Series A. The agents were applied with standard 9-pound Halon 1211 handheld extinguishers pressurized to 190 $lb/in.^2$ with nitrogen gas.

In the Series B tests, a 12-foot-diameter pit having a 100-ft^2 surface area was used. The extinguishers were standard 17-pound handheld Halon 1211 units pressurized to 195 $lb/in.^2$ with nitrogen.

For the Series C tests, the test pit was 20 feet in diameter with a 300-ft^2 surface area. The extinguishers were standard 150-pound wheeled units pressurized to 220 $lb/in.^2$. A constant pressure was applied to the

CAH container during Test Series C. Special nozzles, shown in Figures 1-3, were used for several of these tests. For the other tests, the standard nozzle for the fire extinguisher employed was used.

C. RESULTS

The results, presented in Table 7, indicate that the CFC blend was a good to very good agent. In the largest test, CAH extinguished a fire of a size that Halon 1211 failed to extinguish. The tests indicate that the extinguishing ability of the blend was better for the larger fires. This phenomenon may be due to two factors. First, the blend has some fuel inerting ability, which enables a firefighter to work across a large pool with less burn-back. Second, CAH has a much lower vapor pressure and, therefore, better throw and flame-front penetrating ability than Halon 1211.

For small fires, the extinguishment times for CAH were much longer than those of Halon 1211. The lower vapor pressure for the CFC blend apparently decreases knockdown ability.

TABLE 7. FIELD TEST RESULTS FOR COMMERCIAL CFC BLEND.

Test no.	Agent	Extinguishment time, sec	Agent, lbs	Fuel,[a] gal	Extinguishment
		Test Series A			
1	Halon 1211	3.8	--	2	Yes
2	Halon 1211	3.7	--	0	Yes
[b]3	CAH	9.6	--	1	Yes
[b]4	CAH	9.2	--	0	Yes
		Test Series B			
[c]5	Halon 1211	7.9	11.7	6.25	Yes
6	Halon 1211	2.5	6.7	0	
[b]7	CAH	--	17	3	No[d]
[e]8	CAH	5.3	6.7	0	Yes
[e]9	CAH	--	10.3	4	Yes
		Test Series C			
10	Halon 1211	--	150	18	No[f]
11	CAH	13.8	83.7	18	

[a]Amount added to pool contents from preceding test in same series.

[b]Special nozzle used (Figure 1).

[c]Extinguishment time could have been reduced by improved application.

[d]Extinguishment was not obtained even though all agent was discharged.

[e]Shortened nozzle with enlarged orifice was used (Figure 2).

[f]Fire was allowed to burn to completion before starting the next test.

[g]Nozzle used is shown in Figure 3.

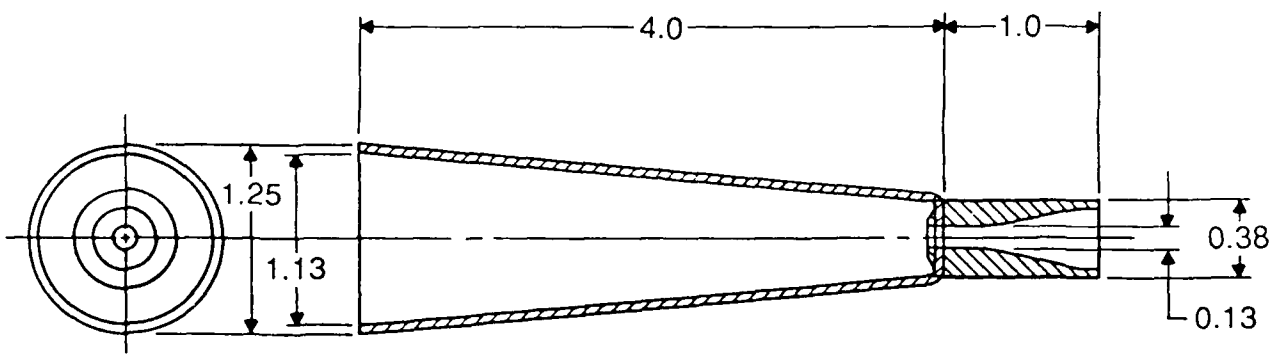


Figure 1. Nozzle Used for Commercial CFC Blend Field Tests 3, 4, and 7.

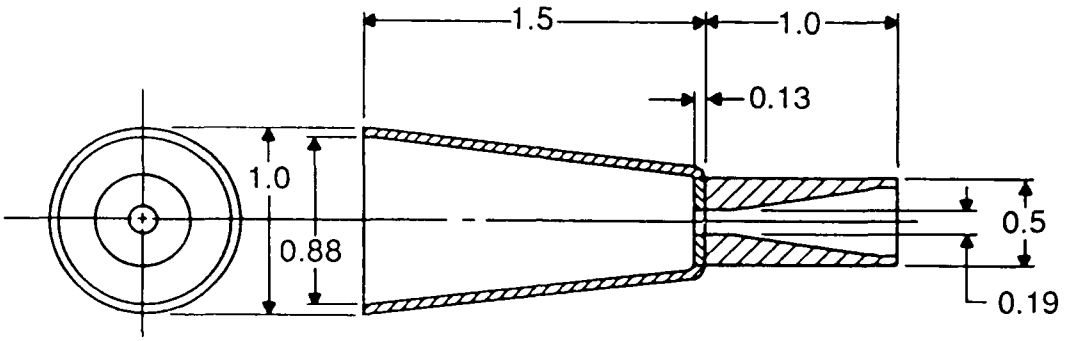


Figure 2. Nozzle Used for Commercial CFC Blend Field Tests 8 and 9.

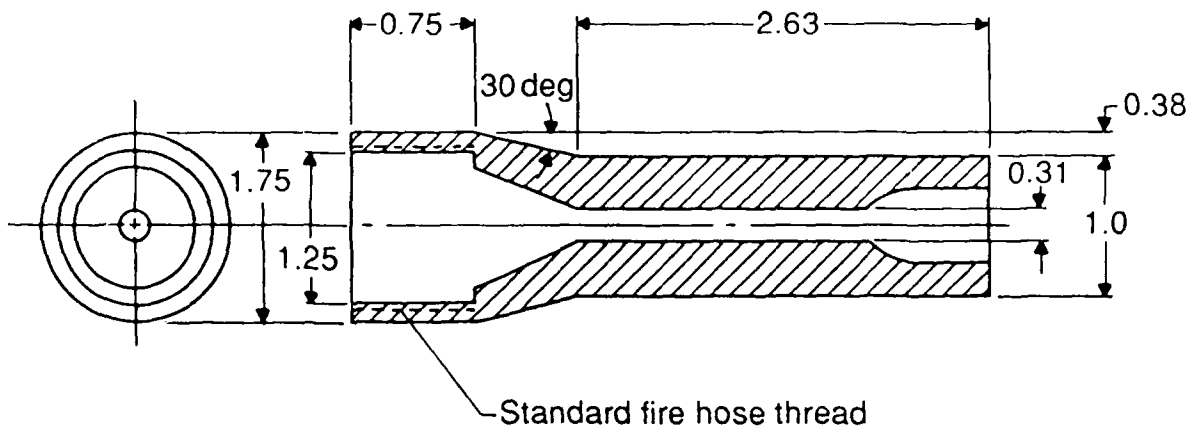


Figure 3. Nozzle Used for Commercial CFC Blend Field Test 11.

SECTION VI
CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Much of the information needed for selection of candidates for alternative training agents and for general halon replacement agents is available. Assessment and interpretation of toxicity data, however, are difficult.

The experimental work performed in Phase IV indicates that a decreased vapor pressure significantly improves agent performance. Evidence of this improved performance is seen in the better extinguishment by HCFC-123 than that of a mixture of HCFC-123 and HCFC-22. The HCFC-22 increases the volatility to the point that the discharge characteristics do not offset the inherently greater concentration needed for extinguishment by HCFCs.

Similarly, the fire suppression ability of a CFC blend, CAH, which has a relatively low vapor pressure, is good to very good in field tests. The extinguishing ability improves as the fire size increases, a consequence of the fuel inerting, discharge, and flame penetrating properties of this agent. On the other hand, the CFC blend lacks rapid fire knockdown capability.

The results from the testing in this phase indicate that a blend of CFCs or HCFCs could provide a replacement for Halon 1211 in firefighter training. However, to approach the fire extinguishment ability of Halon 1211, the vapor pressure of the material must be kept low. A small amount of a more volatile component may give a more rapid fire knockdown, but the addition of too much volatile material can seriously degrade agent performance.

B. RECOMMENDATIONS

1. To handle the large amount of data needed for screening, prioritizing, and selecting candidate agents for halon replacements and alternative training agents, a computerized database of halocarbon properties should be developed.

2. Phase III work indicated the possibility of predicting fire extinguishing capability from molecular formula for halocarbons. An effort in this directions should be pursued.

3. The extreme difficulty in assessing and evaluating toxicity data for halocarbons makes a toxicity database essential in this effort. The database should cover only halocarbons of interest in the halon replacement program. Consideration should also be given to the development of useful toxicity indexes for comparison of candidate agents and to the use of QSARs (Quantitative Structure Activity Relationships) for prediction of acute toxicity from molecular structure and/or physical properties.

4. Investigations should be undertaken to determine which halocarbons are available in large volume, either as products or in process streams.

5. Methods should be developed for the rapid and economical prediction of ODPs from molecular structure without resorting to complex atmospheric models.

6. Since the need still exists for general halocarbon replacements, the Alternative Training Agent program should be broken out into a separate subtask.

REFERENCES

1. Tapscott, R. E., and Morehouse, E. T., Jr., Next-Generation Fire Extinguishing Agent, Phase I - Suppression Concepts, ESL-TR-87-03, Vol. 1 of 5, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, Florida, July 1987.

2. Tapscott, R. E., May, J. H., Moore, J. P., Lee, M. E., and Walker, J. L., Next-Generation Fire Extinguishing Agent, Phase II -- Laboratory Tests and Scoping Trials, ESL-TR-87-03, Vol. 2 of 5, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, Florida, August 1989.

3. Tapscott, R. E., Moore, J. P., Lee, M. E., Watson, J. D., and Morehouse, E. T., Next-Generation Fire Extinguishing Agent, Phase III -- Initiation of Training Agent Development, ESL-TR-87-03, Vol. 3 of 5, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, Florida, August 1989.

4. Van Stee, E. W., A Review of the Toxicology of Halogenated Fire Extinguishing Agents, Report AMRL-TR-74-143, Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, November 1974.

5. Handbook of Chemistry and Physics, R. C. Weast, editor, 64th Edition, CRC Press, Inc., Boca Raton, Florida, p. E-33, 1984.

6. Meyer, Eugene, Chemistry of Hazardous Materials, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, p. 188, 1977.

7. Occupational Safety and Health Standards, Subpart Z - Toxic, Hazardous Substances, 29 CFR 1910.1000.

8. TLVs, Threshold Limit Values and Biological Exposure Indices for 1985-86, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1986.

9. Ember, L. R., Layman, P. L., Lepkowski, W , and Zurer, P. S., "Tending the Global Commons," Chemical and Engineering News, pp. 14-64, 24 November 1986.

10. Chlorofluorocarbons and the Ozone Layer, An Appraisal of the Science, Imperial Chemical Industries, Cheshire, England, October 1986.

11. Molina, M. J., and Rowland, F. S., "Stratospheric Sink for Chlorofluoromethane: Chlorine Atom Catalyzed Destruction of Ozone," Nature, Vol. 249, pp. 810-812, 1974.

12. Wuebbles, D. J., Journal of Geophysical Research, Vol. 88, pp. 1433-1443, 1983.

13. Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling, Evaluation Number 4: NASA Panal for Data Evaluation, National Aeronautics and Space Administration, Jet Propulsion Laboratory Publication 81-3, 15 January 1983.

14. Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling, Evaluation Number 6: NASA Panel for Data Evaluation, National Aeronautics and Space Administration, Jet Propulsion Laboratory Publication 83-62, 15 September 1983.

15. Hammitt, J. K., Wolf, K. A., Camm, F., Mooz, W. E., Quinn, T. H., and Bamezai, A., Product Uses and Market Trends for Potential Ozone - Depleting Substances, 1985-2000, Rand Corporation, R-3386-EPA, May 1986.

16. Mooz, W. E., Wolf, K. A., and Camm, F., Potential Constraints on Cumulative Global Production of Chlorofluorocarbons, Rand Corporation, R-3400-EPA, May 1986.

17. Vogel, T. M., Criddle, C. S., and McCarty, P. L., "Transformations of Halogenated Aliphatic Compounds," Environmental Science and Technology, Vol. 21, p. 722, 1987.

18. Dilling, W. L., Tefertiller, N. B., and Kallas, G. J., "Evaporation Rates and Reactivities of Methylene Chloride Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions," Environmental Science and Technology, Vol. 9, p. 833, 1975.

19. Tomson, M. B., Dauchy, J., Hutchins, S., Curran, C., Cook, C. J., and Ward, C. H., "Groundwater Contamination by Trace Level Organics from a Rapid Infiltration Site," Water Research, Vol. 15, p. 1109, 1981.

20. Walker, T. J., Fate and Disposition of Trichloroethylene in Surface Soils, Ph.D. Dissertation, Available from University Microfilm International, Order No. DA 8500452, 1984.

21. Roberts, P. V., Reinhard, M., and Valocchi, A. J., "Movement of Organic Contaminants in Ground Water: Implications for Water Supply," Journal of the American Water Works Association, Vol. 74, p. 408, 1982.

22. Bear, J., Hydraulics of Groundwater, McGraw-Hill, New York, 1979.

23. Freeze, R. A., and Cherry, J. A., Groundwater, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1979.

24. Weber, W. J., Physiochemical Processes for Water Quality Control, Wiley-Interscience, New York, 1972.

25. Schwarzenbach, R. P., and Westall, J., "Transport of Nonpolar Organic Compounds from Surface Water to Ground Water: Laboratory Sorption Studies." Environmental Science and Technology, Vol. 15, p. 1360, 1981.

26. Urano, K., and Murata, C., "Adsorption of Principal Chlorinated Organic Compounds on Soil," Chemosphere, Vol. 14, p. 293, 1985.

27. Gould, R. F., Editor, "Azeotropic Data III," compiled by L. Horsley, Advances in Chemistry Series 116, American Chemical Society, Washington, D. C., 1973.

U.S. GOVERNMENT PRINTING OFFICE: 1990-736-217/20039 Region 4.

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